ATOMIZED LEAD FREE SOLDER ALLOYS FOR SOLDER PASTE PRODUCT FOR ELECTRONIC APPLICATION

by

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LIST OF ABBREVIATIONS

Bi-In-Sn	:	Bismuth-Indium-Tin
CTE	:	Coefficient of Thermal Expansion
DSC	:	Differential Scanning Calorimetry
EDX	:	Energy Dispersion X-ray
EPA	:	Environmental Protection Agency
EU	:	European Union
IMC	:	Intermetallic Compound
NCMS	:	National Center for Manufacturing Science
OFN	:	Oxygen Free Nitrogen
PCB	:	Printed Circuit Board
PLCC	:	Plastic Leaded Chip Carrier
RoHS	:	Restriction of Hazardous Substances Directive
SEM	:	Scanning Electron Microscopy
SMD	:	Surface Mount Device
SMT	:	Surface Mount Technology
Sn-Pb	:	Tin-Lead
Sn-Zn	:	Tin-Zinc
SOIC	:	Small Outline Integrated Circuit
SOT23	:	Small Outline Transistor
THT	:	Through Hole Technology
XRD	:	X-ray Diffraction
$ZnCl_2$	:	Zinc Chloride

ALOI PATERI BEBAS PLUMBUM BERATOM UNTUK PENGHASILAN PES PATERI BAGI APLIKASI ELEKTRONIK

ABSTRAK

Sifat-sifat aloi-aloi pateri Sn-9Zn dan Bi-48.8In-19.6Sn telah dikaji dengan menggunakan Sn-40Pb sebagai rujukan. Aloi-aloi pateri tersebut dicirikan (ketumpatan, XRD, SEM, CTE dan DSC) sebelum proses pengatoman. Aloi-aloi pateri yang dicirikan kemudiannya diatomkan melalui kaedah gas pada tekanan 0.4 MPa dan suhu panas lampau 20% lebih tinggi daripada suhu pencecairan yang diperolehi daripada analisis DSC. Serbuk pateri kemudian diayak dan dicirikan dengan menggunakan SEM dan penganalisis saiz zarah. Serbuk dengan saiz +75-150 μm yang dicirikan kemudian dicampur dengan fluks zink klorida menggunakan nisbah logam kepada fluks yang berbeza (90:10, 80:20, 70:30, dan 60:40). Sifat-sifat pembasahan (penyebaran dan sudut sentuh), tindak balas antara muka dan sifat mekanikal (ujian ricih) pes-pes pateri kemudiannya dikaji. Pes pateri Sn-40Pb menunjukkan penyebaran tertinggi dan sudut sentuh terendah berbanding dengan Sn-9Zn dan Bi-48.8In-19.6Sn. Pada antara muka pateri/substrat, sebatian antaralogam Cu_6Sn_5 telah terbentuk untuk kedua-dua Sn-40Pb dan Bi-48.8In-19.6Sn tanpa mengambil kira kandungan logam dan sebatian antaralogam Sn-Cu-Zn terbentuk di antara muka Sn-9Zn (90 bt%)/Cu. Kekuatan ricih tertinggi dicapai oleh Sn-9Zn (90 bt%) dengan nilai 45.3 MPa. Kekuatan ricih meningkat dengan peningkatan kandungan logam aloi-aloi pateri Sn-40Pb dan Bi-48.8In-19.6Sn. Kekuatan ricih Sn-40Pb (90 bt%) adalah lebih tinggi daripada kekuatan ricih Sn-40Pb (80 bt%) dan juga sama untuk aloi pateri Bi-48.8In-19.6Sn, di mana kekuatan ricih Bi-48.8In-19.6 Sn (90 bt%) adalah lebih tinggi daripada kekuatan ricih Bi-48.8In-19.6Sn (80 bt%).

ATOMIZED LEAD FREE SOLDER ALLOYS FOR SOLDER PASTE PRODUCT FOR ELECTRONIC APPLICATION

ABSTRACT

Properties of Sn-9Zn and Bi-48.8In-19.6Sn solder alloys have been investigated along with Sn-40Pb as a reference. The solder alloys where characterized (density, XRD, SEM, CTE and DSC) before the atomization process. The characterized solder alloys are then gas atomized at a pressure of 0.4 MPa and superheat temperature of 20% above their respective liquidus temperature obtained from the DSC analysis. Solder powders are then sieved and characterized using SEM and particle size analyzer. The characterized powders of size +75-150 μm are then mixed with zinc chloride flux at different metal to flux ratios (90:10, 80:20, 70:30, and 60:40). The wetting properties (spreading and contact angle), interfacial reactions and mechanical property (shear test) of the solder pastes are then studied. The Sn-40Pb solder paste demonstrates the highest spreading and lowest contact angle compared to Sn-9Zn and Bi-48.8In-19.6Sn. At the solder/substrate interface, the intermetallic compound Cu_6Sn_5 was formed for both Sn-40Pb and Bi-48.8In-19.6Sn regardless of metal content and Sn-Cu-Zn intermetallic compound is formed at the Sn-9Zn (90 wt%)/Cu interface. The highest joint shear strength was achieved by Sn-9Zn (90 wt%) at a value of 45.3 MPa. The shear strength increased as the metal content increases for the Sn-40Pb and Bi-48.8In-19.6Sn solder alloys. The shear strength of Sn-40Pb (90 wt%) is higher than the shear strength of Sn-40Pb (80 wt%) and the same goes for Bi-48.8In-19.6Sn solder alloy where the shear strength of Bi-48.8In-19.6Sn (90 wt%) is higher than the shear strength of Bi-48.8In-19.6Sn (80 wt%).

CHAPTER 1
INTRODUCTION

1.1 Overview

Solder is an interconnect material used in integrated consumer electronic systems. The solder is used to join detached packages to boards and is used to connect the semiconductor die to the package by flip chip or die attach interconnect. The solder acts as a thermal path and joint that holds the parts in place and as an electrical conduit. Solder has excellent thermal and electrical properties by carrying current and heat in an electronic system (Frear, 2007).

The motivation in the search for non-harmful, environmental friendly Pb-free solder alloys in the microelectronic application is to resolve lead-containing solder alloys toxicity to human health and environment. The driving force in search for Pb-free solder alloys is to develop advanced soldering technology for low temperature process and consumers desiring green electronic products. Many electronics consumer companies in Japan have announced their plans to replace Pb-solder connections with Pb-free ones. Numerous Pb-free programs have been initiated in the United States by dedicated societies such as National Electronics Manufacturing Initiative Inc, Association of Connecting Electronics Industries and the Electronics Industries Association (Kang, 2001).

Large amount of harmful materials used in the high-tech industry are encouraging global expansion of the ever changing production lines during the manufacturing process and this is the main cause for depleting natural resources. The ideal situation is to develop the type of technology which is efficient and safe for humans and the environment. Therefore, new legislation is targeting manufacturers of such products containing hazardous substances such as lead (Cannis, 2001).

1.2 Problem Statement

The electronic manufacturing industry fast development has encouraged high usage and high replacement rates among electronics products. This may result in environmental pollution and a direct threat to human life due to short product life cycles and production of growing amounts of electronics waste. The EU's 2003 Restriction of Hazardous Substances Directive (RoHS) as of July 2006, ban the import of electronic products into the EU containing more than specified amounts of hexavalent chromium, lead, mercury, cadmium, polybrominated diphenyl, ethers and polybrominated biphenyls (Chiang et al., 2010).

According to Wood and Nimmo (1994), the Environmental Protection Agency (EPA) listed lead as one of the top element that poses the greatest threat to the environment and human life when used in the electronics industry. The manufacturing of electronic goods contains wide range different substances, some of which are harmful to the environment and to human health especially when leaked into water, soil, and air when not properly recycled. Lead is an element that is used in soldering electronic components on PCBs and is mostly used on computer cameras, key boards, mobile phones, and etc. Improper disposal of electronic products that contains toxic lead is considered hazardous to the environment and human health.

Lead (Pb) has been used in solders for many years due to its low cost and high performance. Of the Pb present in European landfills, 40% originated from consumer electronics. All solders containing lead will be banned in the European Union (EU), due to the potential negative impact of Pb on the environment and on human health. The inflow of Pb in alloys to EU landfills and waste incineration is to about 80% caused by solders used in electronics (Ekvall and Andrae, 2006).

Powder production using a gas atomization process has been being widely applied in industry. Powder produced by gas atomization has many advantages such as high flexibility for both elemental and prealloyed powder production, high capacity, and capability to produce rapidly solidified metal powder. The rapidly solidified metal powders usually exhibit superior properties such as fine microstructure, chemical homogeneity, and metastable phase formation compared to other powder production methods such as the tear drop method (Monnapas et al., 2010). With solder powder being a key component in solder paste, powder produced by atomization can improve the overall performance of solder paste in SMT.

The thermal–mechanical characteristics of solder joints are vital to the design and use of reliable PCBs and to the development and assessment of product reliability. Leaded solder has numerous advantages over lead-free solder. The liquidus temperature of solder in general is a key issue in manufacturing of printed circuit boards as damage to electronic components occur at higher temperatures as well as issues with intermetalic compound (IMC) growth. Sn-37Pb is a eutectic alloy which produces eutectic microstructure on solidification, has good wettability and forms a smooth bright finish. The goal of most solder manufacturing companies is to find a replacement of lead containing solders with properties similar to leaded solder as leaded solder has good solderability, wetting properties and mechanical properties (Moshrefi-Torbati and Swingler 2010).

1.3 Objective of the Research

Research on properties of lead free solder alloys has increased in scope, size and area in the high-tech electronic industry specifically in the Surface Mount Technology (SMT) application. Hence, the main goal of this research is to investigate the properties of tin-zinc (Sn-9Zn) solder, bismuth-indium-tin (Bi-48.8In-19.6Sn) solder and tin-lead (Sn-40Pb) solder. The main objectives of this research are:

1- To develop lead free solder powders based on Sn-9Zn, Bi-48.8In-19.6Sn and Sn-40Pb systems by using gas atomization method.
2- To characterize atomized lead-free solder powders and develop suitable metal to flux ratios as candidate for lead-free solder paste.
3- To study the physical and mechanical properties on newly developed lead-free solder pastes.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

Soldering is defined as the joining of metals by utilizing another metal, which has a melting point or range below about 450°C and is lower than the metals to be joined. This differs from brazing, in which the added metal generally has a melting range above 450°C, but also below the metals to be joined. Solders are typically classified as either soft or hard. Soft solders typically consist of alloys containing lead and tin, but also often contain indium (In), bismuth (Bi), antimony (Sb), or silver (Ag). Most soft alloys melt at temperatures lower than 450°C, usually between 180°C and 300°C. High-tin solders, typical of lead-free solders, tend to be stiffer, harder, and less ductile compared to high lead solders. Hard solders often contain metals such as Au, Al, and Si (Puttlitz, 2004).

During the soldering process, the parts to be joined are heated at temperature higher than the liquidus temperature, causing complete melting of the solder and formation of bond to the materials to be joined by wetting action. After the metal cools, the resulting joints is weaker than the base metal, but have sufficient electrical conductivity and strength. Soldering is different from welding in which the base are metals not being melted during the joining process and from brazing by use of a lower melting-temperature filler metal.

Solder interconnect reliability is the prospect of the solder interconnects to perform the intended functions such as electrical conductivity, thermal tolerance and withstand the tensile and shear stresses for a prescribed product life, under applicable use conditions such as temperature, voltage, current density, humidity, static and dynamic mechanical loading, and corrosion without failures. Failures may manifest themselves in many different modes, such as mechanical, electrochemical, and may possibly occur at various systems interconnection locations such as, substrates, components and/or solder joints (Shangguan, 2005).

The elimination of the usage of Pb solders due to toxicity of lead in electronic assemblies has been targeted by environmental regulations around the world. These environmental regulations have pushed forward the development of Pb free solders. Successful Pb free alloys replacements need to be reliable over the long run to replace Pb solders. Although many of the Pb-free solder alloys have superior strength than the Sn-Pb, there still exist reliability problems such as poor wettability, creep and electromigration (Wu et al., 2004).

2.2 Tin-Lead Solder Alloy

The 20th century ushered in the era of electronics in which Sn-Pb solders had their most far reaching role. The first electrical connections in early radio and telecommunications equipment were mechanical attachments. The application of solder to those connections prevented them from loosening, thereby reducing static in signal transmission and reception. The low melting temperature eutectic and near-eutectic compositions, 63Sn-37Pb, 50Sn-50Pb, and 60Sn-40Pb were used for these applications. Whether through-hole solder joints or advanced surface mount technology, soldering with Sn-Pb alloys has remained as the primary assembly methodology in the electronics industry today. The material systems used in electronic devices, components, and sub-assemblies have been specifically developed for processing with one or more of the Sn-Pb alloys (Vianco, 2004).

Lead-bearing solders had become the largest group of alloys utilized in electronics products; among these were eutectic 63Sn-37Pb and near-eutectic 60Sn-40Pb solders used extensively for PCB assemblies (Puttlitz, 2004). Lead plays a very important role in Sn-Pb solder alloys and in solder joints of electronic assemblies. Pb does not participate in the formation of any intermetallic compounds, neither at the terminal ends of solder joints nor distributed within the bulk solder. It reduces the melt temperature of alloys with Sn, improves the mechanical characteristics of Sn as a solder joint material by reducing stiffness and increasing plasticity without significantly affecting solder interactions between Sn and terminal metallizations, namely Cu and Ni (Harrison et al., 2001).

The Sn-Pb binary system has a eutectic reaction around 183°C with a composition of 63Sn-37Pb (wt%). The eutectic reaction is taken as the following form (Liang et al., 2007):

Liquid phase (L) $\rightarrow$ β Sn (solid solution with Pb, tetragonal lattice) + α Pb (solid solution with Sn, BCC lattice).

The solubility of the eutectic Sn-Pb solder alloy is 2.5% of Pb in Sn and 19% of Sn in Pb. The Sn solubility in Pb reduces considerably to less than 2% at room temperature, while Pb solubility in Sn is reduced to literally zero. Sn-Pb solders with compositions other than eutectic will have primary Tin-rich phase for Tin-rich solders which forms dendrites or primary lead phase for Pb rich solder or, with subsequent precipitations of saturated Pb or Tin phases within these primary phases. Figure 2.1 shows the eutectic diagram for tin-lead solder.

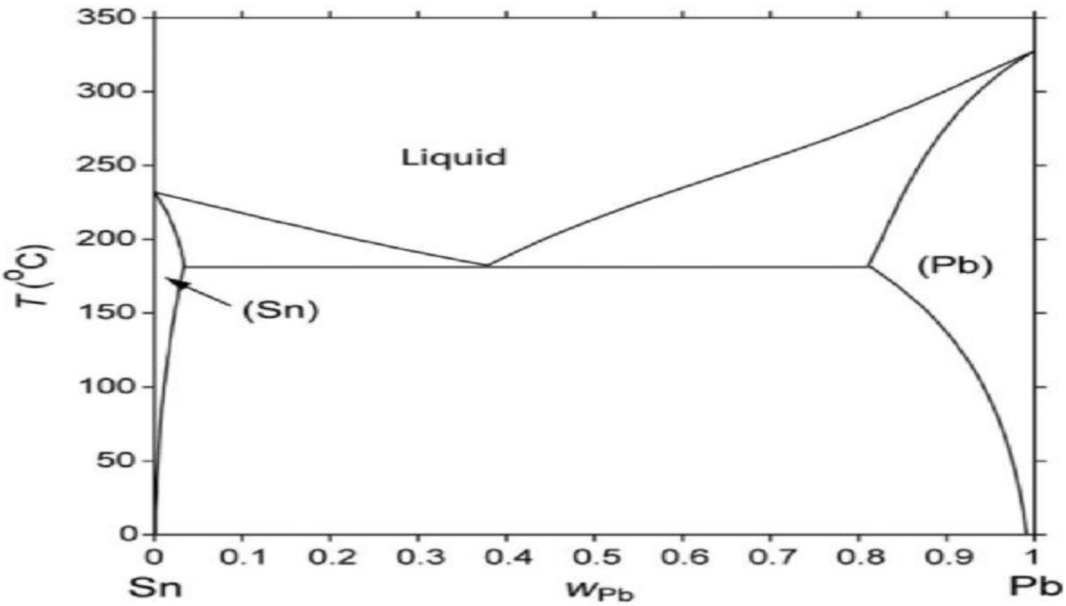

Figure 2.1: Sn-Pb phase diagram (Bath, 2007)

The lead-tin system only has one chemically active element, tin (Sn). All the bonds with the contact material that Sn-Pb solders form do so by the formation of intermetallic compounds (IMCs) containing only Sn. Lead (Pb) however does lower the surface tension value of molten Sn-Pb, which is the driving force behind the excellent wetting and spreading characteristics of Sn-Pb solders (Puttlitz and Galyon, 2007).

2.3 Lead Free Solder

Most Pb-free solders are Sn-based. A particular class is the eutectic alloys of Sn and noble metals: Au, Cu, and Ag. A eutectic alloy is used as solder because it has a single low melting point. Thus, the entire solder joint will melt or solidify at a temperature; otherwise partial melting or solidification may occur. Other alloying elements such as In, Zn, Sb, Bi, and Ge have been considered as eutectic partner with

Sn. Due to its reactivity, germanium is used only in small quantity as an alloying element of multi-component solders. Ternary and higher order solders are most expected to be based on the binary eutectic, Sn–Cu, Sn–Zn, Sn–Ag or Sn–Bi alloys (Zeng and Tu, 2002).

The ability of Sn to spread and wet on a wide range of substrates, using a wide range of fluxes has caused it to become a major component of most solder alloys used for electronic applications. Sn exists in two different forms and crystal structures in the solid state. White (β-tin) and gray (α-tin) which are stable below 13°C. The change of β-tin to α-tin is known as tin pest, and takes place when the temperature falls below 13°C and results in a large increase in volume, which can induce cracking in the tin structure (Abtew and Selvaduray, 2000).

The progress in development of lead-free solder materials without harmful components such as lead has received much awareness in recent years. The primary reason for this is the restriction by legislations on the use of lead in microelectronics. Additionally, new lead-free solders developed by various consortia can offer improved properties and broaden the current range of application of the soldering technology. A candidate solder alloy must be able to possess properties such as good wettability, able to form of strong chemical bond with the a variety of substrates, good electrical conductivity, suitable solidification properties, suitable melting temperature, good mechanical properties, safe for environment and low material cost (Chriastelová and Ozvold, 2008).

Table 2.1: Pass-Fail criteria used by the NCMS Pb-Free solder project (Bath, 2007)

Solder property	Definition	Acceptable levels
Liquidus temperature	Temperature at which solder alloy is completely molten.	< 225°C
Pasty range	Temperature difference between solidus and liquidus temperatures; temperature range where the alloy is part solid and part liquid.	< 30°C
Wettability	A wetting balance test assesses the force resulting when a copper wire is immersed in and wetted by a molten solder bath. A large force indicates good wetting, as does a short time to attain a wetting force of zero and a short time to attain a value of two-thirds of the maximum wetting force.	Fmax > 300 μN t0 < 0.6 s t2/3 < 1 s
Area of coverage	Assesses the coverage of the solder on Cu after a typical dip test.	>85% coverage
Thermo - mechanical fatigue	Cycles-to-failure for a given percent failed of a test population based on a specific solder-joint and board configuration, compared to eutectic Sn-Pb.	Some percentage, usually > 50%
Coefficient of thermal expansion (CTE)	Thermal expansion coefficient of the solder alloy is the fraction change of length per temperature change. Value used for comparison was CTE of solder alloy at room temperature.	< 2.9 x 10^{-5}°C
Creep	Stress required at room temperature to cause failure in 10,000 minutes.	> 3.4 MPa
Elongation	Total percent elongation of material under uniaxial tension at room temperature.	> 10%

Bath (2007) stated that the National Center for Manufacturing Science (NCMS) Pb-Free Solder Project completed in 1997, the required criteria for candidate alloys, as seen in Table 2.1, were created to represent practical restrictions on maximum temperature, requirements in thermo-mechanical fatigue life, reflow temperature, mechanical strength, wetting and oxidation of the molten solder alloy.

Process technologies currently in use for Sn-Pb solder alloy or other Pb-containing solders must be compliant to the new lead free solder without major changes and investments. The new solder wettability should be equivalent or better to that of Sn-Pb solder and a better or equivalent defect rate in the assembly line should be achievable. It should be practical to use with a wide range of fluxes. The new solder liquidus temperature is required to be lower than those of the present solders to minimize thermal stresses or thermal shock during soldering. To meet basic requirements such as oxidation, reliability and corrosion, the new solder must produce solder joints with adequate joint strength and withstand thermal fatigue over the anticipated operating life of the assembly (Kang, 1999).

2.3.1 Tin-Zinc (Sn-Zn) Solder Alloy

Sn-Zn solder alloy has been considered as a potential candidate for lead-free solder because its melting temperature of 198°C which is relatively close to that of eutectic Sn-Pb solder, superior mechanical properties compared to Sn-Pb solders and lower cost compared to lead-free solders.

During the manufacturing of electronic interconnections when using Sn-Zn solders, an aggressive flux or protective atmosphere is needed (Huang and Lin 2006). The phase diagram of Sn-Zn is shown in Figure 2.2.

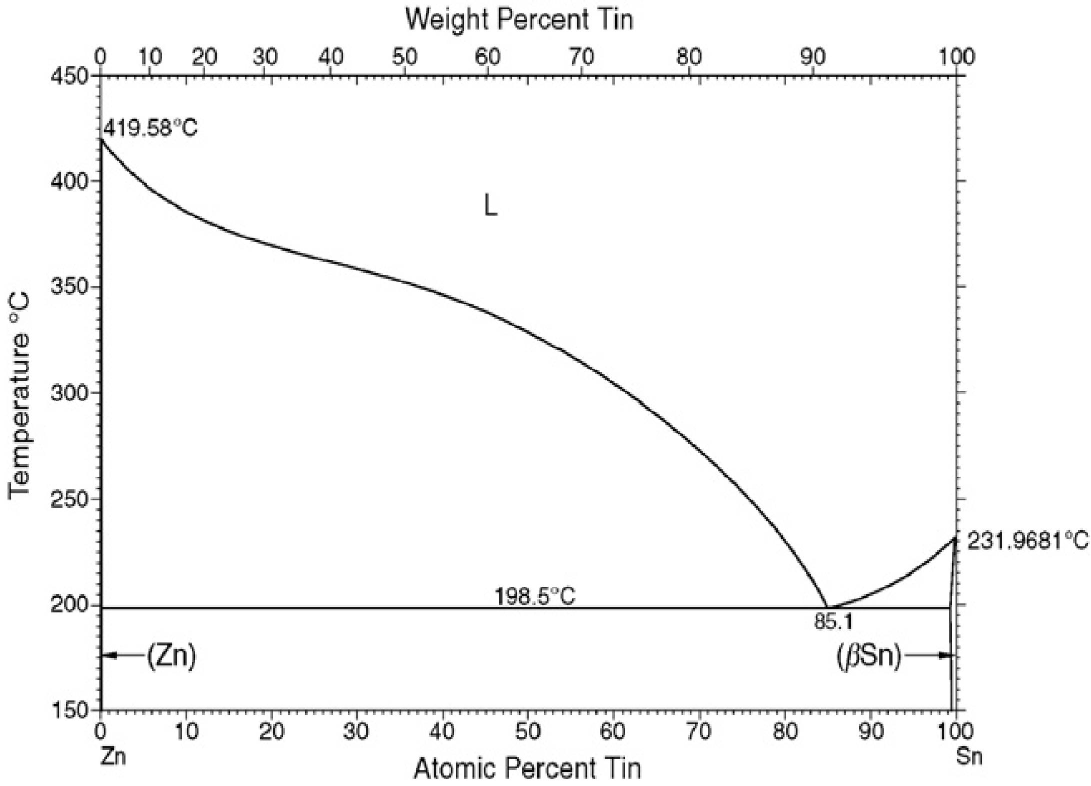

Figure 2.2: Sn-Zn phase diagram (Wei et al., 2007)

Abtew and Selvaduray (2000) stated that the eutectic structure of Sn-Zn consists of two phases: Sn matrix phase and a secondary phase of Zn containing less than 1% tin in solid solution. The microstructure of Sn-Zn system is reported to exhibit large grains with a fine uniform two-phase eutectic colony and an expected lamellar microstructure. Sn-9wt% Zn is the eutectic composition for the Sn-Zn system (Figure 2.2) consisting of alternating Zn rich and Sn rich phases.

2.3.2 Bismuth-Indium Tin (Bi-In-Sn) Solder Alloy

Bi-In-Sn solder alloy is a good low temperature lead-free solder alloy and technologically important for soldering applications. Bi-In-Sn solder has low melting temperature, good wettability and good mechanical properties. The Bi-In-Sn solder alloy has low liquidus temperature which can be used in low temperature soldering. Additionally, its low liquidus temperature permits it's usage in new generation of nano silicon chips, organic-based transistor such as liquid crystal display, and in polymeric conductive boards. This alloy can also be used in outer space nano satellites under cryogenic conditions (minus 147-447°C) (Noor et al., 2010).

Calculated liquidus temperature of Bi-In-Sn system that is suggested by (Moelans et al., 2003), is shown in Figure 2.3. There is only one eutectic point marked as E shown in Figure 2.3. This eutectic point is important in producing solder alloy which can melt at a single temperature.

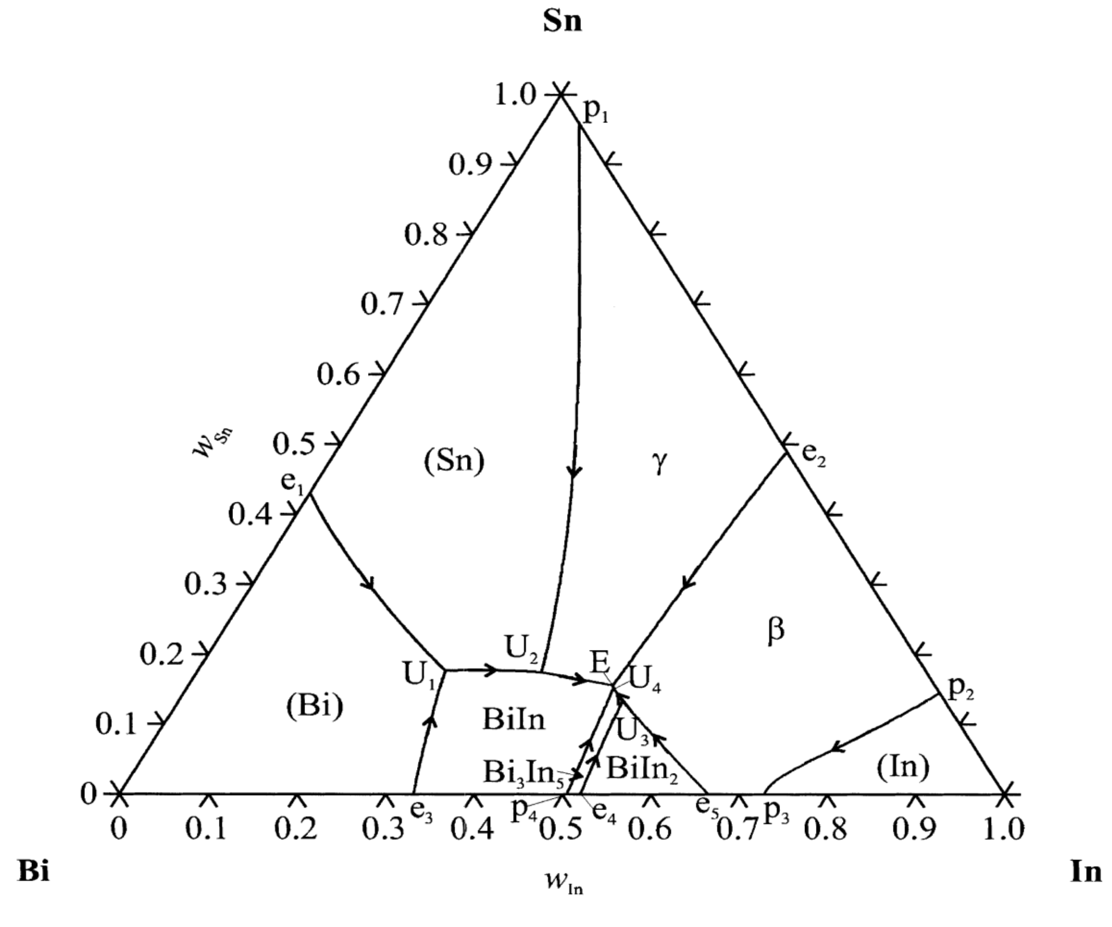

Figure 2.3: Bi-In-Sn phase diagram (Moelans et al., 2003)

2.4 Soldering Technology

2.4.1 Reflow Soldering

Reflow soldering is a process of joining PCB with electrical components by heating the PCB and the solder paste so that the solder paste melts, wets and then solidifies to form the solder joints. Soldering can be attained through various heat-transfer modes such as conduction, induction, convection, vapour condensation, infrared convection, laser beam, resistance, and hot gas. Each soldering method has its advantages and disadvantages in cost, performance, and operational efficiency depending on product quantity and materials. Sn-Pb solders require lower soldering temperatures compared to Pb-free solders. Board materials and components must be able to withstand the higher temperatures to avoid damage (Kwon, 2007). An example of reflow soldering profile is shown in Figure 2.4, and the phases of reflow soldering are (Blackwell, 2006) :

- Preheating: The substrate, components, and solder paste are preheated.
- Drying: Solvents evaporate from the solder paste. Flux activates, reduces oxides, and evaporates. Both low and high-mass components have enough soak time to reach temperature equilibrium.
- Reflow: The solder paste temperature exceeds the liquidus point and reflows, wetting both the component leads and the board pads. Surface tension effects occur, minimizing wetted volume.
- Cooling: The solder paste cools below the liquidus point, forming shiny and appropriate volume solder joints.

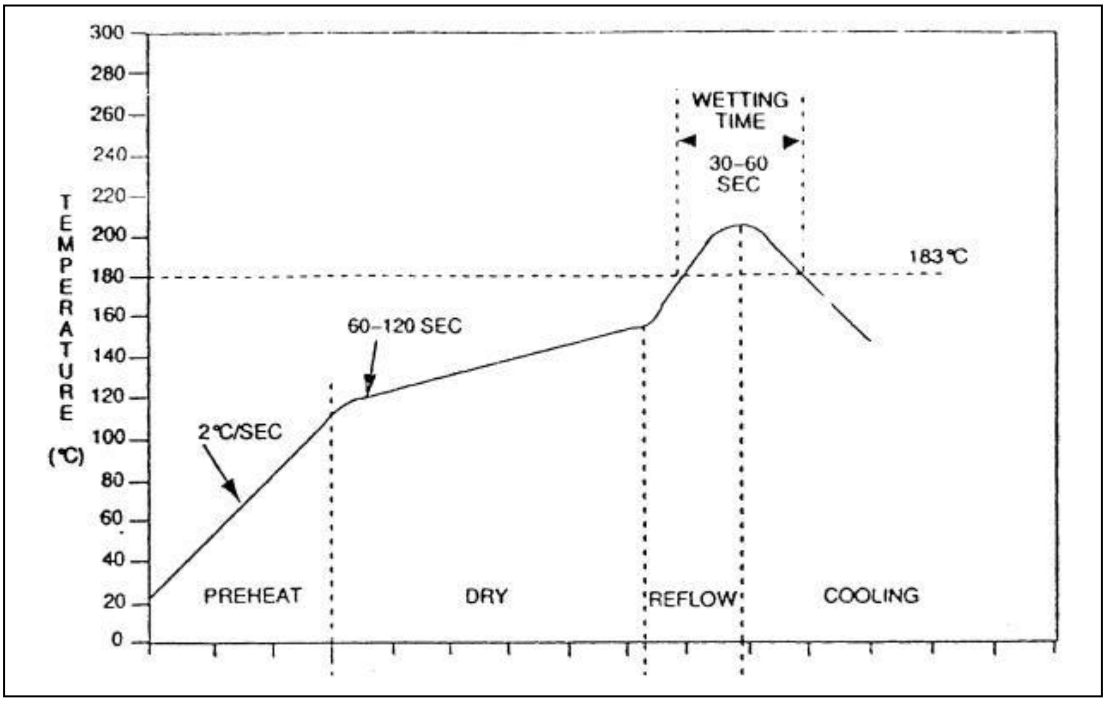

Figure 2.4: Typical thermal profile for SMT reflow soldering (Blackwell, 2006)

Recommended reflow profile for semiconductor components developed by IPC/JEDEC is shown in Table 2.5. These recommended profiles are based on the temperature taken at the top-side of the packaged device (Turbini, 2007). These recommendations are based on package volume excluding external leads, or solder balls in the case of ball grid arrays (BGAs) and non-integrated heat sinks.

Table 2.2: Reflow profiles recommended for Sn/Pb and Pb-free assemblies (Turbini, 2007)

Profile feature	Sn-Pb assemblies	Pb-free assemblies
Average ramp-up rate	3°C/s max	3°C/s max
Preheat - Temperature min - Temperature max - Time	 100°C 150°C 60–120 s	 150°C 200°C 60–180 s
Time maintained above melting temperature	60–150 s	60–150 s
Time within 5°C of peak Temperature	10–30 s	20-40 s
Ramp down rate Time 25°C to peak temperature	6°C/s max 6 min max	6°C/s max 8 min max

2.4.2 Wave Soldering

Wave soldering is a method used to create joints for through-hole configurations and solder chip components. Wave soldering process has been in use for many years with Sn-Pb solder due to its cost advantages and productivity for high-volume products (Kwon, 2007).

Key wave soldering processes include fluxing, preheating and soldering. Fluxing the electronic assemblies by the application of flux. The preheater heats the board before soldering. Every joint carries only the optimum amount of solder to produce an effective joint. Preheating is employed before actual wave soldering to raise the temperature of the board, activate the flux, reduce the number of blowholes in the solder joint and reduce thermal shock to the board from the solder wave. The boards, once fluxed and preheated, are soldered by a solder wave. Wave soldering depends on many parameters that affect the overall performance of the soldering system such as flux density, foam head, solder alloy, solder temperature, conveyor parallelism, oil adjustment, dross level, solder wave and smoothness of the wave (Pecht, 1993). Figure 2.5 shows a wave profile for a VOC-free flux.

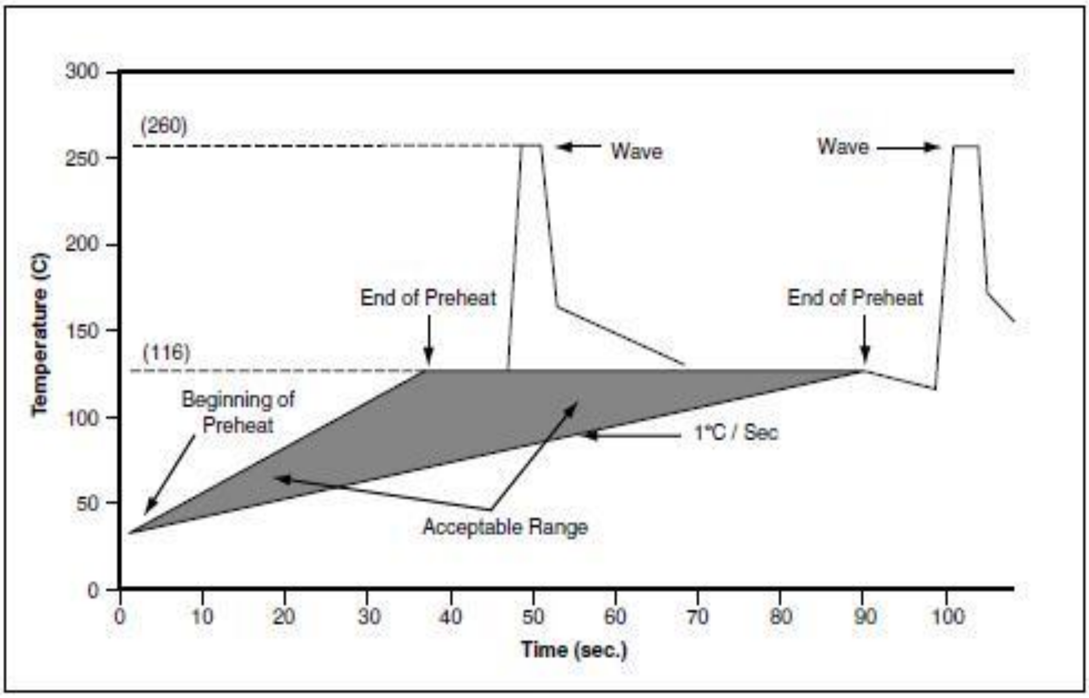

Figure 2.5: Typical wave soldering thermal Profile (Faure and Bath 2007)

Pin through-hole soldering is carried out by wave soldering as shown in Figure 2.6, where the assembly is transported over a molten solder bath from which the solder rises and forms solder joints by capillary action (Abtew and Selvaduray, 2000). The important properties of the solder are always process dependent. The density and viscosity of the molten solder are key parameters that influence the process of the wave soldering.

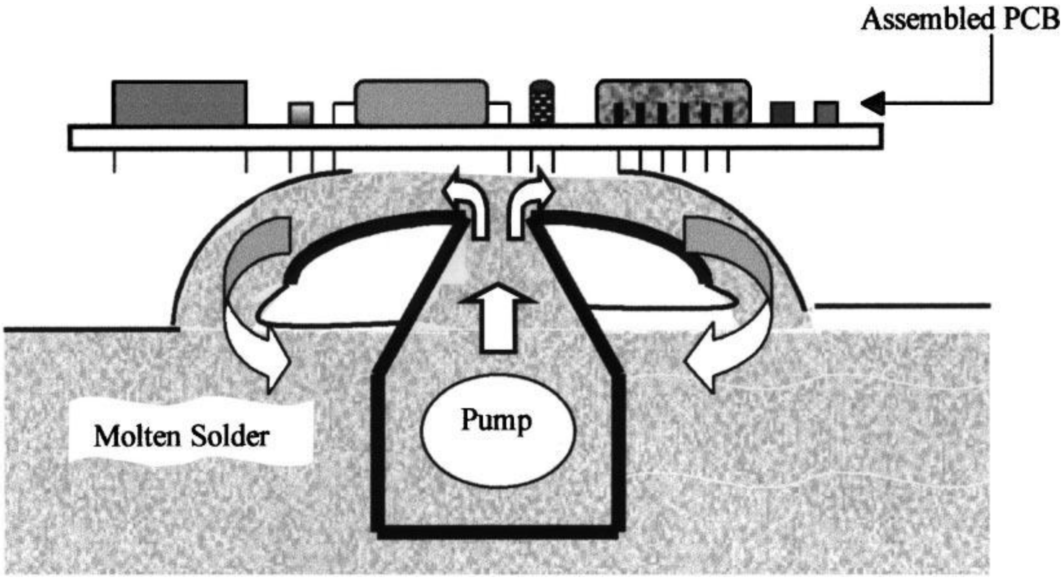

Figure 2.6: Wave soldering of a PCB (Abtew and Selvaduray 2000)

2.5 Solder Paste

Solder paste can be defined as a mixture of solder metal powder and flux. Solder paste is a key material in surface mount technology (SMT). An ideal solder paste will increase production yields while decreasing the amount of defects related with reflow soldering. The performance of a paste, however, depends on a range of factors such as storage, printability, rheology, tackiness, ability to avoid reflow defects and reliability (Nguty and Ekere, 2000a). The performance parameters of solder paste before soldering, during soldering and post soldering are listed in Table 2.3.

Table 2.3: Solder paste performance parameters (Lau, 1991)

Stage	Parameter
Before soldering	- Physical appearance - Cold lump - Tack time - Screen and stencil printability
During soldering	- Compatibility with surface to be joined - Wettability - Flow property at and before molten - Solder Balling Phenomenon - Leaching phenomenon
Post soldering	- Residue quality - Residue cleanability - Electromigration - Joint appearance - Joint strength - Joint microstructure

Solder paste consists of solder alloy powder generally produced by atomization techniques, flux and vehicle carrier system. It can be classified as a homogeneous mixture or as a dense suspension. As a dense suspension of 50% solid and 50% liquid by volume, it has inherent characteristics such as volume fraction, size distribution, metal content, inter-particle forces and possible particle-flux interaction. To be described as a homogeneous and kinetically stable mixture, solder paste is characterized by properties such as viscosity, normal forces, surface tension and density (Nguty and Ekere, 2000b).

The solder paste production process needs some complicated operations such as powder production and selection, vehicle preparation, paste mixing which strongly affect the paste performance. At least five compounds make up vehicle, whereas fluxes are commonly made of natural chemicals (Lapasin et al., 1994).

2.5.1 Solder Flux

Since the 1980's, solder fluxes have gone through tremendous changes. In the past, soldering fluxes were rosin-based and they are traditionally categorized to military specifications: R - rosin, RMA - rosin mildly active, RA - rosin active and RSA - rosin super activated. As well as water soluble fluxes used for some applications. In the past, most fluxes contained 25 to 30% solids where as new flux formulations use weak, often non-clean organic acids and have much lower solids content (1.5–5 %) (Turbini, 2007).

Fluxes used for soldering in the microelectronic industry with Sn-Pb alloys have been largely based on resin-based mixtures. Rosin is a natural product derived from pines trees consisting of roughly 80% of resin acids with a chemical formula $C_{19}H_{29}COOH$. Lead-free soldering processes require higher operational temperature and has lower wettability compared to conventional Sn-Pb solder alloys. The flux in electronic applications used with lead-free solder alloys will require higher flux capacity, higher oxygen barrier capability, and higher thermal stability in comparison with fluxes used with Sn-Pb solder alloys (Arenas et al., 2006).

Flux is needed for soldering processes to provide oxide removal from substrate surface, heat transfer, and improve wetting. The degree of wetting depends on the surface cleanliness as well as on the interfacial tensions of the solid/liquid contact systems. The liquid/flux and solid/flux interfacial tensions vary with respect to composition, flux type, and temperature (Yu et al., 2000).

Turbini (2007) stated that metal surfaces to be joined must be clean of oxidation and contamination for the soldering process to take place. When flux is heated, the cleaning action takes place to promote the formation of an intermetallic layer, minimizes oxidation of the basis metal and removes surface oxidation. The flux usually consists of:

- Activators: React with and remove the metal oxides.
- Vehicle: Coats the surface to be soldered, dissolves the metal salts produced when the activator reacts with the oxides, and provides a covering for the cleaned metal surface to prevent further oxidation until soldering takes place.
- Solvent: Dissolves the activators and vehicle and deposits them uniformly on the board and component surfaces.
- Special additives: Rheological agents and other special ingredients are added to fluxes used in solder pastes, paste flux, and cored wire flux.

During soldering process, the vehicle and wetting agents (solvents) are lost through volatilization at the elevated temperature. Upon completion of the soldering process, a residue may remains on the part surface. This residue reflects the flux's solids contents. Higher solid contents result in a greater extent of residues that remains on the base materials surface after completion of the soldering process. In rosin based fluxes, solid contents are typically 35-46%, but can be as high as 57%. Low residue fluxes have 2-6% solid contents. The functions of flux during the fabrication of a solder joint are elimination of the oxide layer from the base metal surface to provide the molten solder with high surface tension which is the driving force for solder spreading, reduce the surface tension of the molten solder which assists in the spreading of solder on horizontal and vertical surfaces. Fluxes also establish a barrier between the base metal surface and the atmosphere during soldering process. The flux prevents the reoxidation of the base metal during the preheat step of the soldering process which preceeds the formation of the joint by the molten solder (Vianco, 1999).

2.6 Gas Atomization

Gas atomization is the process in which the liquid metal is dispersed by a high-velocity jet of argon, air, helium or nitrogen. Gas atomization is used for the commercial production of powders of copper, copper alloys, aluminium and its alloys, magnesium, zinc, titanium, titanium alloys, nickel-base alloys, cobalt-base alloys, lead, tin, solder, precious metals, refractory metals, beryllium, etc. In conventional gas-atomization processes, the atomization pressures are typically in the range 0.5 to 4 MPa and Mach 1 to 3 gas velocities in the nozzles. Typically, gas-atomized powders are usually spherical with average particle sizes are usually in the range 10 to 300 µm (Neikov, 2009).

As illustrated in Figure 2.7, during free fall spray forming, the molten metal is released from the bottom of the crucible through a nozzle. The molten metal stream travels downwards through the atomizer unit, until it is atomized at a certain point below the nozzle tip of the atomizer. This free fall spray forming set up prevents the freeze up of molten metal. Close couple atomizer is more prone to freeze up due to the nozzle being in close contact with the atomizing gas.

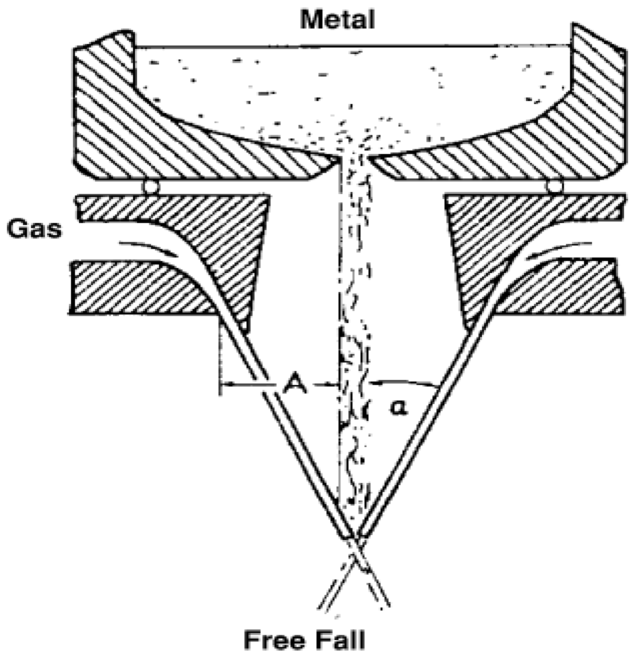

Figure 2.7: Typical arrangement of a free fall spray forming (Monnapas et al., 2010)

2.7 Solder Alloys Properties

2.7.1 Melting Point

Polymeric materials are used as PCB materials based on cost considerations, cannot withstand high temperature for long time. They tend to char and decompose under such conditions. To achieve suitable solderability conditions, soldering operation requires molten solder by 40°C to 50°C above liquidus temperature. In high volume applications, electronic solders melting point upper limit is set at about 230°C. Eutectic Sn-Pb suited for these considerations with a melting point of 182°C which well below the upper limit for melting point. Melting point of lead-free solders under consideration are in range of 200 - 230°C (Subramanian and Lee 2003).

According to Abtew and Selvaduray (2000), melting point of eutectic Sn-Pb solder is 183°C which represents 40°C of operational margin. The typical solder reflow temperature is 220°C. If polymeric materials can endure highest temperature of 250°C for a period of 120s without degradation, then the use of a solder alloy with higher liquidus temperature is achievable if 20°C margin is sufficient. It becomes possible to use solder alloys with liquidus temperatures 230°C. The acceptable highest liquidus temperature would be dependent on the following factors:

- Polymeric materials used in microelectronics can endure the highest temperature, without the onset of permanent degradation.
- The efficiency of heat transfer to ensure that the solder alloy melts, forms a joint, and resolidifies within a reasonable time so that productivity can be maintained.
- The extent to which the temperature profile variations inside the ovens used for soldering can be controlled with precision

Low processing temperature is required during soldering of electronic devices to prevent heat damage. This is the reason for the adoption of low melting alloys with melting temperature below 150°C (Chriastelová and Ozvold, 2008). If the peak operational reflow temperature used during electronic devices soldering is reduced, thermally induced damages will be reduced. A considerable decrease in the peak reflow temperature would reduce damage to components. Peak reflow temperatures are around 210°C to 230°C for present operational reflow temperature. These temperatures are sufficient to cause popcorning that usually occur in reflow soldering, in which air and moisture that absorbed by the plastic package of an IC are heated to the point where they expand and cause the component case to crack open (Zequn Mei, 1996).

2.7.2 Wetting

Solderability is dependent upon the wettability of two surfaces being joined is crucial to the efficiency of manufacturing and the reliability of electronic devices (Seung W. Y. et al., 1999). Wettability is generally described by the contact wetting angle θ, to the substrate as shown in Figure 2.8.

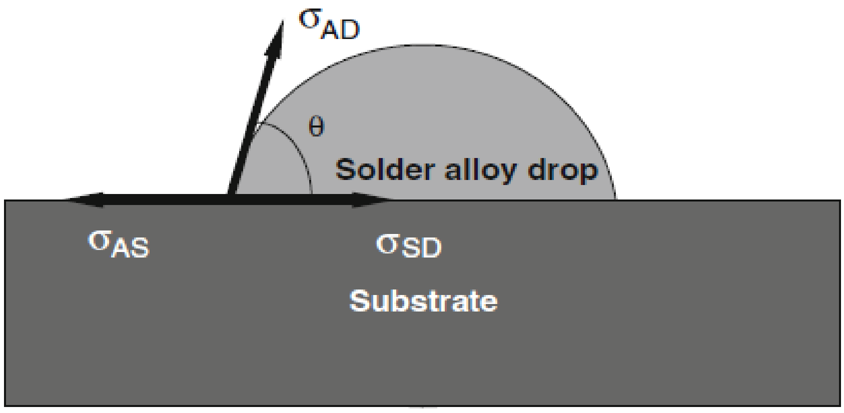

Figure 2.8: Schematic representation of the contact angle (θ) between an alloy drop and a substrate (Garcia et al., 2009)

Solder wettability can be measured by measuring the contact angle of wetting. In addition to the type of flux used, the measurement of the contact angle values involves a number of parameters that have an impact on the results, such as surface roughness, time, and temperature. The contact angles for Pb-free solder alloys show that the reported values are quite hard to compare to each other, due to the different conditions used during testing (Arenas et al., 2006).